

**REMARKS**

Claims 113-119 are pending in this application. Claim 113-119 are amended for clarity by replacing the term "hydrogel composition" with "solution", the term "hydrogel" with "polymer hydrogel", Claims 113-114 further amended by adding the phrases "the solution of the polymer hydrogel gels *in situ* after injection" and "for injection into a body cavity" for additional clarity. Support for the amendment can be found throughout the specification, see for example, page 5, lines 26-27; paragraph bridging pages 5 and 6; page 9, lines 8-21; paragraph bridging pages 16-17; and page 38, lines 15-28. Therefore, no new matter is introduced. The Office Action is discussed below:

***Anticipation/Obviousness Rejections:***

On pages 2-3 of the Office Action, the examiner has maintained the rejection of claim 113 allegedly as being anticipated by Hyon (US 4,663,358) or Yamauchi (JP 03215417).

The examiner also has maintained the rejection of claims 113-119 allegedly as being anticipated by or, in the alternative, as being obvious over Tanihara (US 5,880,216), KU (US 5,981,826), Yao (US 6,268,405), or Okamura (JP 04338326).

Applicants respectfully disagree with the examiner and traverse the rejections for the reasons discussed below.

***Response to Arguments:***

Regarding the declaration filed 03/02/2007, the examiner asserts that the term "injectable", as defined in the declaration (being limited to being injectable through a 5.57 mm artifice under 11 lbs or a 20 cc syringe at 45 psi) is not disclosed in the specification or in the claims. Thus, the examiner concludes that the declaration is not commensurate in scope with what is actually being claimed. Applicants respectfully disagree with the examiner and clarify that for the sake of demonstration, the experiment as described in the declaration was carried out based on the usual injection

pressure employed by anesthesiologists (which is ~25 psi, which is 172 kPa or 450 g of load for the 5.75 mm orifice). Applicants refer to Claudio *et al.*, *Regional anesthesia and Pain Medicine* (2004) 29(3) pp 201-205 (abstract). Applicants also refer to U.S. Patent No. 6,533,819 (see for example, col. 8, line 61-67, col. 9, 1-9) for a general definition of the term "injectable", which relates to materials having a texture and viscosity which permits their flow through a suitable surgical needle or other surgical instrument, such as a equipment used in endoscopic or percutaneous discectomy procedures, by employing typical injection pressures. For example, an injectable material of low viscosity can be forced through at least the diameter of a 22-gauge needle. As indicated above, in the declaration, parameters were chosen to demonstrate that under reasonable conditions, as defined in the relevant literature representative of the field, a freeze-thaw hydrogel was not injectable. Applicants did not mean to demonstrate an example including all possible conditions disclosed in the specification. Applicants, however, demonstrated that a freeze-thaw processed hydrogel is not injectable. Therefore, one skilled in the art would understand the "injectable" polymer hydrogel as recited in the claims. The parameters chosen for the demonstration were purely exemplary, based on what is known in the art and with no intention to limit the scope of the instant claims.

The examiner also asserts that the concentration and type of hydropolymer used in the declaration are not commensurate in scope with independent claim 113. Again, the applicants disagree with the examiner and submit that the examples in the declaration are to show that a temperature-cycled PVA hydrogel is not injectable with clinically-relevant loads. Applicants clarify that the 15% PVA in DI (as shown on Figures 10 through 12 of the declaration exhibits) is not in accordance with the instantly claimed process but was used as an example, as described above.

On page 4 of the Office Action, regarding Hyon *et al.*, Ku *et al.*, Yao *et al.*, Okamura and Tanihara *et al.*, the examiner states that the limitation that the hydrogel be prepared without "the physically cross-linked hydrogel is formed without chemical cross-linkers, irradiation or thermal cycling", this limitation refers to the process, which is not what is currently being claimed. The examiner asserts that the applicant still has not

demonstrated that the process used in the references, even if different from that of applicant's, would necessarily result in products materially different from what is currently claimed and originally presented. Applicants disagree with the examiner and point out that the Hyon *et al.*, Ku *et al.*, Yao *et al.*, Okamura and Tanihara *et al.* processes do not yield a product according to the claimed invention, for example the instant product is physically and structurally different and are a result of different processes. Therefore, Hyon *et al.*, Ku *et al.*, Yao *et al.*, Okamura or Tanihara *et al.* processes does not anticipate the claimed invention nor a combination thereof renders the claimed invention obvious.

Regarding the PVA copolymer in Tanihara *et al.*, the examiner believes that a PVA copolymer is still a PVA polymer and, in this case, still a PVA polymer hydrogel. Applicants respectfully disagree with the examiner, refer to the response filed on March 2, 2007 and reiterate that Tanihara disclosure is not relevant to the claimed invention. Tanihara does not describe a PVA hydrogel because the commonly understood definition of a PVA polymer is one with the majority of monomeric groups consisting of  $-CH_2-CHOH-$ , depending on hydrolyzation of saponification level. The name, PVA is an acronym for poly(vinyl alcohol) and therefore technically requires a molecule that is composed of vinyl alcohol monomers. The "PVA" described by Tanihara contains structural units at mole fractions of 0.05 to 0.5 of the formula I and/or formula II in that patent, and is thus termed a 'copolymer' by those familiar in the art, and cannot be simply described as "PVA" (see col. 3, line 64 through col. 4, line 21). Tanihara claims a wound dressing material of hydrogel containing HA or HA-salt (see claims 1 & 2). The material described by Tanihara is however not a PVA polymer, and is instead a molecule with a specific pendant group (see formula I).

Applicants further clarify that PVA is defined as the molecule with the vinyl alcohol monomer with some percentage of vinyl acetate and does not refer to PVA copolymers. Applicants refer to the following web-links for additional clarity (also see attached are hard copies from the web-links):

[http://en.wikipedia.org/wiki/Polyvinyl\\_alcohol](http://en.wikipedia.org/wiki/Polyvinyl_alcohol)

<http://www.socplas.org/industry/defs.htm>.

Applicants indicate that the above entries discuss required modification of PVA in order to make copolymers. Additionally, applicants provide, for example, see Sigma Aldrich source, where there are 39 grades of PVA available, but any molecule that is PVA based with modification is cited as a copolymer.

Moreover, Tanihara requires:

Process 1 (see column 16, line 51), which involves simultaneous or sequential modification of polyvinyl alcohol, thus the product is no longer a polymer; and

Process 2 (see column 17, line 19) is described as “[t]he homopolymer or copolymer thus is partially saponified... Then, the hydroxyl group of the saponified product produced by saponification is modified to a final 0.0001 to 0.5 molar fraction range...”

Hence, Tanihara disclosure relates to copolymers resulting from the modification by above described processes 1 or 2. Therefore, Tanihara disclosure is not relevant to the claimed invention.

On page 5 of the Office Action, the examiner opined that the claimed invention must result in a structural difference between the claimed invention and the prior art in order to patentably distinguish the claimed invention from the prior art. In response applicants reiterate that the claimed final products are physically and structurally different than those of the cited arts, for example, claimed products are injectable while none of the final products according to the cited references are injectable.

The examiner refers that “some of the prior art hydrogels are solid and therefore not injectable”, is not a persuasive arguments and contends that Tanhara *et al.*, Ku *et al.*, Okamara and Hyon hydrogels are in both liquid and article forms. Applicants respectfully disagree with the examiner and refer to the arguments as filed on March 2, 2007, that none of the cited references provide a final product that is injectable. More specifically, see response filed on March 2, 2007, for example page 10, that describes “the final article is a solid hydrogel, which cannot be injected (see [Tanihara] col. 16, line 48 through col. 21 line 47, for process of making the modified gel and its characteristics usable as wound dressing but not as an injectable hydrogel).”

Applicants further note that the polymer solutions of the claimed invention is formed without use of any chemical cross-linkers and explain that the lack of chemical cross-linking treatment allows the instantly claimed polymer solutions to be "injectable." As submitted in the earlier response and herein that none of cited the prior art hydrogels that are prepared without a freeze-thaw cycle lack chemical cross-linker. Therefore, the claimed injectable solutions are chemically and structurally different from the prior art hydrogels.

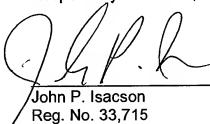
However, without acquiescing in the rejection, in order to expedite the prosecution, applicants amend claims 113-119 for clarity by replacing the term "hydrogel composition" with "solution", without prejudice or disclaimer.

In view of the above response, applicants request withdrawal of the anticipation and obviousness rejections.

**REQUEST**

Applicants submit that claims 113-119 are in condition for allowance and respectfully request favorable consideration to that effect. The examiner is invited to contact the undersigned at (202) 416-6800 should there be any questions.

Respectfully submitted,

  
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July 30, 2007

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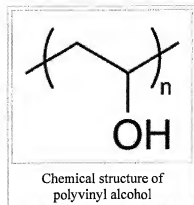
# Polyvinyl alcohol

From Wikipedia, the free encyclopedia

**Polyvinyl alcohol** (**PVOH**, **PVA**, or **PVAL**) is a water-soluble synthetic polymer.

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## Properties

Polyvinyl alcohol has excellent film forming, emulsifying, and adhesive properties. It is also resistant to oil, grease and solvent. It is odorless and nontoxic. It has high tensile strength, flexibility, as well as high oxygen and aroma barrier. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticiser, will then reduce its tensile strength, but increase its elongation and tear strength.

PVA has a melting point of 230°C and 180–190°C for the fully hydrolysed and partially hydrolysed grades. It decomposes rapidly above 200°C as it can undergo pyrolysis at high temperatures.

PVA is an atactic material but exhibits crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it.

## Uses

Some uses of polyvinyl alcohol include:

1. Adhesive and thickener material in latex paints, paper coatings, hairsprays, shampoos and glues.
2. Carbon dioxide barrier in polyethylene terephthalate (PET) bottles.
3. Carotid phantoms for use as synthetic vessels in doppler flow testing.
4. Children's play putty or slime when combined with borax.
5. Feminine hygiene and adult incontinence products as a biodegradable plastic backing sheet.
6. As a mold release because materials such as epoxy do not stick to it.
7. As a water-soluble film useful for packaging.
8. As fiber reinforcement in concrete
9. As a surfactant for the formation of polymer encapsulated nanobeads
10. Used with polyvinyl acetate to make Elmer's glue
11. Used in eye drops as a lubricant.

## Fishing

PVA is widely used in freshwater sport fishing. Small bags made from PVA are filled with dry- or oil-based bait and attached to the hook, or the baited hook is placed inside the bag and cast into the water. When the bag lands on the lake or river bottom it breaks down, leaving the hook bait surrounded by ground bait, pellets etc. This method helps attract fish to the hook bait, though it does result in dissolved plastic in the water.

Anglers also use string made of PVA for the purpose of making temporary attachments; for example holding in a coil a length of line that might otherwise tangle while the cast is made.

## Production

There are over 22 producers worldwide with ~ 1 million tons on the open market in 2002. Larger producers include Kuraray (Japan) and Celanese (USA) but mainland China has installed a number of very large production facilities in the past decade.

## Preparation

Unlike most vinyl polymers, PVA is not prepared by polymerization of the corresponding monomer. The monomer, vinyl alcohol, almost exclusively exists as the tautomeric form, acetaldehyde. PVA instead is prepared by partial or complete hydrolysis of polyvinyl acetate to remove acetate groups.

## External links

- Chemical properties (<http://www.jtbaker.com/msds/englishhtml/p5282.htm>)
- Listed as a plastic by the Society of the Plastics Industry (<http://www.socplas.org/industry/defs.htm>)
- "Slime" recipe (<http://chem.lapeer.org/chem1docs/SlimeDemo.html>)
- Forming PVA layers in PET bottles (<http://www.pslc.ws/macrog/iblend.htm>)

Retrieved from "[http://en.wikipedia.org/wiki/Polyvinyl\\_alcohol](http://en.wikipedia.org/wiki/Polyvinyl_alcohol)"

Categories: Vinyl polymers | Biodegradable plastics | Polymer stubs

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## definitions of plastic resins

**PLASTICS** have developed an amazing presence in our lives. From the most commonplace tasks to our most unusual needs, plastics increasingly have provided the performance in products that consumers want. In fact, if you woke up tomorrow and there were no plastics, you would be in for quite a shock. Life would be much more expensive and much less comfortable. And many of the conveniences you had come to take for granted would be gone. Mostly, though, you would be surprised at the many products that had vanished—things you had never thought of as being plastic. That's because, in just a few decades, consumers have come to consider the extraordinary properties of plastics as nothing out of the ordinary. Plastics' popularity and wide usage can be attributed to one basic fact: Because of their range of properties and design technologies, plastics offer consumer benefits unsurpassed by other materials. Let's take a look at the different types of plastics, usually referred to as "resins," and see how they are made and used:

Plastics generally are organic high polymers (i.e., they consist of large chainlike molecules containing carbon) that are formed in a plastic state either during or after their transition from a small-molecule chemical to a solid material. Stated very simply, the large chainlike molecules are formed by hooking together short-chain molecules of chemicals (monomers: mono = one, mer = unit) in a reaction known as polymerization (poly = many). When units of a single monomer are hooked together, the resulting plastic is a homopolymer, such as polyethylene, which is made from the ethylene monomer. When more than one monomer is included in the process, for example, ethylene and propylene, the resulting plastic is a copolymer.

### Thermosets and Thermoplastics

The two basic groups of plastic materials are the thermoplastics and the thermosets. Thermoplastic resins consist of long molecules, each of which may have side chains or groups that are not attached to other molecules (i.e., are not crosslinked). Thus, they can be repeatedly melted and solidified by heating and cooling so that any scrap generated in processing can be reused. No chemical change generally takes place during forming. Usually, thermoplastic polymers are supplied in the form

of pellets, which often contain additives to enhance processing or to provide necessary characteristics in the finished product (e.g., color, conductivity, etc.). The temperature service range of thermoplastics is limited by their loss of physical strength and eventual melting at elevated temperatures.

Thermoset plastics, on the other hand, react during processing to form crosslinked structures that cannot be remelted and reprocessed. Thermoset scrap must be either discarded or used as a low-cost filler in other products. In some cases, it may be pyrolyzed to recover inorganic fillers such as glass reinforcements, which can be reused. Thermosets may be supplied in liquid form or as a partially polymerized solid molding powder. In their uncured condition, they can be formed to the finished product shape with or without pressure and polymerized by using chemicals or heat.

The distinction between thermoplastics and thermosets is not always clearly drawn. For example, thermoplastic polyethylene can be extruded as a coating for wire and subsequently crosslinked (either chemically or by irradiation) to form a thermoset material that no longer will melt when heated. Some plastic materials even have members in both families; there are, for instance, both thermoset and thermoplastic polyester resins.

## PLASTIC RESINS

### Acetal

An engineering thermoplastic introduced to industry in 1956 as a potential replacement for die-cast metals. Acetal resins are produced by the polymerization of purified formaldehyde [ $\text{CH}_2\text{O}$ ] into both homopolymer and copolymer types. Industrial end-users are very familiar with the acetals in the form of gears, bearings, bushings, cams, housings, conveyors and any number of moving parts in appliances, business machines, etc.,. Consumers may be more familiar with applications such as automotive door handles, seat belt components, plumbing fixtures, shaver cartridges, zippers and gas tank caps. Acetals are extremely rigid without being brittle. They have a high melting point, high strength, good frictional properties and resistance to fatigue.

### Acrylics

Were introduced in 1936 in the form of hard, rigid and transparent materials. Acrylics were used in World War II as aircraft canopies. Other applications include: lighting diffusers; outdoor signs; automobile tail lights; washbasins and sinks; safety shields; furniture (e.g., tables); skylights, and large-area enclosures for shopping centers, swimming pools, restaurants, etc., and as room dividers. The outstanding resistance

to long-term exposure to sunlight and weathering is one of the more important characteristics of acrylic. Also notable is the exceptional clarity and good light transmission (cast acrylic sheet transmits about 92% total light). Acrylics are a family of thermoplastic resins of acrylic esters  $[\text{CH}_2\text{CHCOOR}]$  or methacrylic esters  $[\text{CH}_2\text{C}(\text{CH}_3)\text{COOR}]$ . The acrylates may be methyl, ethyl, butyl, or 2-ethylhexyl. Usual methacrylates are the methyl, ethyl, butyl, laural and stearyl.

### Acrylonitrile-Butadiene-Styrene (ABS)

Chemically, this family of thermoplastics are called terpolymers, because they are made of three different monomers: acrylonitrile, butadiene and styrene, to create a single material that draws on the best properties of all three. ABS was introduced to the market in 1948, primarily as a result of activities that had taken place during the war years in the development of synthetic rubbers. ABS possesses outstanding impact strength and high mechanical strength, which makes it suitable for use in tough consumer and industrial products, including: appliances, automotive parts, pipe, business machines and telephone components. In the 1960s, ABS found wide outlet as a substrate for metallizing (i.e., applying a chrome-like metallic finish to the plastic) and appeared in such products as shower heads, door handles, faucet handles and automotive front grilles. A class of thermoplastic terpolymers including a range of resins, all prepared with usually more than 50% styrene  $[\text{C}_6\text{H}_5\text{CHCH}_2]$  and varying amounts of acrylonitrile  $[\text{CH}_2\text{CHCN}]$  and butadiene  $[\text{CH}_2\text{CHCHCH}_2]$ . The three components are combined by a variety of methods involving polymerization, graft copolymerization, physical mixtures and combinations thereof.

### Alkyds

This plastic was developed in 1926 and was promptly put to work in liquid form as enamels, paints, lacquers, and similar coatings for automobiles, refrigerators, stoves and similar products--still the largest use for alkyds. In 1948, however, an alkyd compound was introduced as a molding material for compression molding electrical applications like circuit breaker insulation, coil forms, capacitor and resistor encapsulation, cases, housings, and switchgear components. Major properties are in the electrical area where alkyd molding materials offer excellent dielectric strength. Alkyds also have excellent heat resistance and are dimensionally stable under high temperatures. Alkds are thermosetting unsaturated polyester resins produced by reacting an organic alcohol with an organic acid, dissolved in and reacted with unsaturated monomers such as styrene  $[\text{C}_6\text{H}_5\text{CHCH}_2]$ , diallyl phthalate  $[\text{C}_6\text{H}_4(\text{COOCH}_2\text{CHCH}_2)_2]$ , diacetone acrylamide  $[\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{CHCHCONH}_2]$  or vinyl toluene  $[\text{CH}_2\text{CHC}_6\text{H}_4\text{CH}_2]$ . Typical applications are electrical uses, automotive parts, and as coatings.

### Cellulosics

Cellulosics go back to the very start of the plastics industry when John Wesley Hyatt created the first commercial U.S. plastic, cellulose nitrate, in 1868. Several other important members of the cellulosics family, each with its distinct properties, were introduced in the 1900s. Since then, cellulosics have been used to make knobs, appliance housings, handles, toys, packaging, consumer products, and automotive parts, among many other products. Cellulosics are thermoplastic resins manufactured by chemical modification of cellulose  $[(C_6H_{10}O_5)_n]$ . Included are:

cellophane—regenerated cellulose made by mixing cellulose xanthate  $[ROCSSH]$  with a dilute sodium hydroxide  $[NaOH]$  solution to form a viscose, then extruding the viscose into an acid bath for regeneration; cellulose acetate—an acetic acid ester  $[CH_3COOC_2H_5]$  of cellulose; cellulose acetate butyrate—a mixed ester produced by treating fibrous cellulose with butyric acid  $[CH_3CH_2CH_2COOH]$ , butyric anhydride  $[(CH_3CH_2CH_2CO)_2O]$ , acetic acid  $[CH_3COOH]$  and acetic anhydride  $[(CH_3CO)_2O]$  in the presence of sulfuric acid  $[H_2SO_4]$ ; cellulose propionate—formed by treating fibrous cellulose with propionic acid  $[CH_3CH_2CO_2H]$  and acetic acid and anhydrides in the presence of sulfuric acid; cellulose nitrate—made by treating fibrous cellulosic materials with a mixture of nitric  $[HNO_3]$  and sulfuric acids.

### Coumarone-Indene

Thermoplastic resin obtained by heating mixtures of coumarone  $[C_8H_6O]$  and indene  $[C_6H_4CH_2CHCH]$  with sulfuric acid  $[H_2SO_4]$  to promote polymerization. These resins have no commercial applications when used alone. They are used primarily as processing aids, extenders and plasticizers with other resins in asphalt floor tile.

### Diallyl Phthalate (DAP)

The term DAP is used both for the monomeric and polymeric forms. The monomer  $[C_6H_4(COOCH_2CHCH_2)_2]$  is used as a cross-linking agent in unsaturated polyester resins. As a polymer, it is used in the production of thermosetting molding powders, casting resins and laminates.

### Epoxy

Epoxyes are used by the plastics industry in several ways. One is in combination with glass fibers (i.e., impregnating fibers with liquid epoxy resins) to produce high-strength composites or reinforced plastics that provide heightened strength, electrical and chemical properties, and heat resistance. Typical uses for epoxy-glass reinforced plastics are in aircraft components, filament wound rocket motor casings for missiles, pipes, tanks, pressure vessels and tooling jigs and fixtures. Epoxyes are also used in the encapsulation or casting of various electrical and electronic components and in the powder coating of metal substrates. Major outlets

for epoxies also include adhesives, protective coatings in appliances, industrial equipment, gymnasium floors, etc., and sealants. Epoxies are thermosetting resins that, in the uncured form, contain one or more reactive epoxide or oxirane groups. These epoxide groups serve as cross-linking points in the subsequent curing step, in which the uncured epoxy is reacted with a curing agent or hardener. Cross-linking is accomplished through the epoxide groups as well as through hydroxyl groups that may be present. Most conventional unmodified epoxy resins are produced from epichlorohydrin (chloropropylene oxide)  $[\text{CH}_2\text{OCHCH}_2\text{Cl}]$  and bisphenol A  $[(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2]$ . The other types of epoxy resins are phenoxy resins, novolac resins, and cycloaliphatic resins.

### Fluoropolymer

Fluoropolymers are known for their inertness to most chemicals, resistance to high temperatures, extremely low coefficients of friction and excellent dielectric properties which are relatively insensitive to temperature and power frequency. Typical applications for fluoropolymers are electrical/ electronic uses and pipe and chemical processing equipment and non-stick coatings for cookware and other applications. Fluoropolymers make up a family of thermoplastic resins analogous to polyethylene in which some of the hydrogen atoms attached to the carbon chain are replaced by fluorine or fluorinated alkyl groups. In some cases, other halogens such as chlorine are also part of the molecule. The most common commercial fluoropolymers are: FEP (fluorinated ethylene-propylene) from tetrafluoroethylene  $[\text{C}_2\text{F}_4]$  and hexa-fluoropropylene  $[\text{C}_3\text{F}_6]$ ; PTFE (polytetra fluoroethylene) from the polymerization of tetrafluoroethylene and ethylene  $[\text{C}_2\text{H}_4]$ ; PFA (perfluoroalkoxy) from tetrafluoroethylene and perfluoropropyl vinyl ether  $[\text{C}_3\text{H}_7\text{C}_4\text{OF}_5]$ ; PCTFE (polychlorotrifluoro-ethylene) from chlorotrifluoro-ethylene monomer  $[\text{C}_2\text{F}_3\text{Cl}]$ ; CTFE-VDF (polychlorotrifluoroethylenevinylidene fluoride) from chlorotrifluoroethylene and vinylidene fluoride  $[\text{C}_2\text{H}_2\text{F}_2]$ ; E-CTFE (polyethylenchlorotrifluoroethylene) from chlorotrifluoroethylene and ethylene; PVDF (polyvinylidene fluoride) from vinylidene fluoride monomer; and PVF (polyvinyl fluoride) from vinyl fluoride monomer  $[\text{C}_2\text{H}_3\text{F}]$ .

### Melamine-Formaldehyde

This plastic is a member of the amino family (which also includes urea) and is probably best known to the public as colorful, rugged dinnerware. However, it also finds use in many household goods, in various electrical applications, and in bonding, adhesives and coatings. products. Melamines offer extreme hardness, excellent colorability and arc-resistant nontracking characteristics. Thermosetting resins formed by the condensation reaction of formaldehyde  $[\text{HCHO}]$  and melamine  $[\text{C}_3\text{N}_3]$

$(\text{NH}_2)_3$ ]. The chemistry is analogous to that of ureaformaldehyde except that the three amino groups of melamine provide more possibilities for cross-linking, are more highly reactive, and all six hydrogen atoms of melamine will react, forming the hexamethyl compound.

### Nitrile Resins

This family of resins started to appear in the late 1960s and early 1970s. They are called barrier resins since one of their prime attributes is their resistance to the transmission of gas, aroma or flavor, making them useful in packaging applications. These thermoplastic resins are composed of acrylonitrile  $[\text{CH}_2\text{CHCN}]$  along with comonomer such as acrylates, methacrylates, butadiene  $[\text{CH}_2\text{CHCHCH}_2]$  and styrene  $[\text{C}_6\text{H}_5\text{CHCH}_2]$ . Both straight copolymers and copolymers grafted onto elastomeric backbones are available.

### Nylon

The nylon fiber industry was born in 1939 when 64 million pairs of nylon stockings were sold--and to this day, most people still associate nylon with fibers. However, in the 1940s and 1950s work continued on developing nylon compounds that could be molded and extruded or otherwise processed like plastics. Typical applications for nylons are in automotive parts, electrical/electronic uses, and packaging. Nylon is a generic name for a family of long-chain polyamide engineering thermoplastics which have recurring amide groups  $[-\text{CO}-\text{NH}-]$  as an integral part of the main polymer chain. Nylons are synthesized from intermediates such as dicarboxylic acids, diamines, amino acids and lactams, and are identified by numbers denoting the number of carbon atoms in the polymer chain derived from specific constituents, those from the diamine being given first. The second number, if used, denotes the number of carbon atoms derived from a diacid. Commercial nylons are as follows: nylon 4 (polypyrrolidone)-a polymer of 2-pyrrolidone  $[\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{NH}]$ ; nylon 6 (polycaprolactam)-made by the polycondensation of caprolactam  $[\text{CH}_2(\text{CH}_2)_4\text{NHCO}]$ ; nylon 6/6-made by condensing hexamethylenediamine  $[\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2]$  with adipic acid  $[\text{COOH}(\text{CH}_2)_4\text{COOH}]$ ; nylon 6/10-made by condensing hexamethylenediamine with sebacic acid  $[\text{COOH}(\text{CH}_2)_8\text{COOH}]$ ; nylon 6/12-made from hexamethylenediamine and a 12-carbon dibasic acid; nylon 11-produced by polycondensation of the monomer 11-amino-undecanoic acid  $[\text{NH}_2\text{CH}_2(\text{CH}_2)_9\text{COOH}]$ ; nylon 12-made by the polymerization of laurolactam  $[\text{CH}_2(\text{CH}_2)_{10}\text{CO}]$  or cyclododecalactam, with 11 methylene units between the linking  $-\text{NH}-\text{CO}-$  groups in the polymer chain.

### Petroleum Resins

Thermoplastic resins obtained from a variable mixture unsaturated

monomers recovered as byproduct from cracked and distilled petroleum streams. They also contain indene [ $C_6H_4CH_2CHCH$ ], which is copolymerized with a variety of other monomers including styrene [ $C_6H_5CHCH_2$ ], vinyl toluene [ $CH_2CHC_6H_4CH_3$ ], and methyl indene [ $C_6H_3CH_3CH_2CHCH$ ]. Typical applications are adhesives, printing inks, rubber compounding, and surface coatings.

### Phenolic

These thermosetting resins are credited with being the first commercialized wholly synthetic polymer or plastic, and the second major plastic (the first being cellulose nitrate). The basic raw materials are formaldehyde [ $HCHO$ ] and phenol [ $C_6H_5OH$ ], although almost any reactive phenol or aldehyde can be used. The phenols used commercially are phenol, cresols [ $CH_3C_6H_4OH$ ], xylenols [ $(CH_3)_2C_6H_3OH$ ], p-t-butylphenol [ $C_4H_9C_6H_4OH$ ], p-phenylphenol [ $C_6H_5C_6H_4OH$ ], bisphenols [ $(C_6H_4OH)_2$ ], and resorcinol [ $C_6H_4(OH)_2$ ]. The aldehydes used are formaldehyde and furfural [ $C_4H_3OCHO$ ]. In the uncured and semi-cured condition, phenolic resins are used as adhesives, casting resins, potting compounds, and laminating resins. As molding powders, phenolic resins can be found in electrical uses. They are also used in such applications as: automotive distributor caps, fuse blocks and connectors and appliance handles, knobs and bases. Phenolic is the most popular binder for holding the various plies of wood together in plywood.

### Polyamide-Imide

Engineering thermoplastic resins produced by the condensation reaction of trimellitic anhydride [ $OCC_6H_2C_2O_3$ ] and various aromatic diamines. Typical applications are in the aerospace, automotive and heavy equipment industries.

### Polyarylates

Can be used for automotive, appliance and electrical applications requiring outstanding heat resistance. They are engineering thermoplastic resins produced by interfacial polymerization of an aqueous solution of the disodium salt of bisphenol A [ $(CH_3)_2C(C_6H_4OH)_2$ ] with phthalic acid chlorides [ $C_6H_4(CO)_2Cl_2$ ] in methylene chloride ( $CH_2Cl_2$ ). The major use of polyarylates is in outdoor lighting.

### Polybutylene

Thermoplastic resins offering high flexibility, resistance to creep, cracking and most chemicals. Polybutylene is produced via stereospecific Ziegler-Natta polymerization of butene-1 monomer [ $CH_2CHCH_2CH_3$ ]. Typical applications are pipe and packaging film.

### Polycarbonate

Polycarbonates were developed commercially in 1957 and are one of the pioneering members of the family of "engineering thermoplastics" created to compete with die-cast metals. They are strong, tough and rigid, while having the ductility normally associated with softer, lower-modulus thermoplastics. They also have excellent electrical insulating characteristics, maintained over a wide range of temperatures and loading rates. Polycarbonates are transparent and can be processed in a variety of ways, including injection molding, extrusion, blow molding and rotational molding. Typical applications are glazing, appliances, water bottles and electrical uses. Polycarbonates are engineering thermoplastic resins produced by (1) phosgenation of dihydric phenols, usually bisphenol A  $[(CH_3)_2C(C_6H_4OH)_2]$ , (2) ester exchange between diaryl carbonates and dihydric phenols, usually between diphenyl carbonate  $[(C_6H_5O)_2CO]$  and bisphenol A and (3) interfacial polycondensation of bisphenol A and phosgene  $[COCl_2]$ .

### Polyethylene

This plastic came to the fore during the World War II years, first as an underwater cable coating, then as a critical insulating material for such vital military applications as radar cable. It was not until the end of the war that the plastic was taken off allocation and freed for consumer use. From that point on, its rise in popularity for both consumer and industrial uses was so spectacular that polyethylene became the first plastic in the U.S. to sell more than 1 billion pounds a year. Today, it is still the largest volume plastic in the United States; in fact, it is the largest in the world. Applications for polyethylenes are many and varied, including: packaging films; trash, garment, grocery and shopping bags; molded housewares; toys; containers; pipe; drums; gasoline tanks; coatings and many others. Polyethylenes are thermoplastic resins obtained by polymerizing the gas ethylene  $[C_2H_4]$ . Low molecular weight polymers of ethylene are fluids used as lubricants; medium weight polymers are waxes miscible with paraffin; and the high molecular weight polymers (i.e., over 6000) are the materials used in the plastics industry. Polymers with densities ranging from about .910 to .925 are called low density; those of densities from .926 to .940 are called medium density; and those from .941 to .965 and over are called high density. The low density types are polymerized at very high pressures and temperatures, and the high density types at relatively low temperatures and pressures. A relatively new type called linear low density polyethylene is manufactured through a variety of processes: gas phase, solution, slurry, or high pressure conversion. A high efficiency catalyst system aids in the polymerization of ethylene and allows for lower temperatures and pressures than those required in making conventional low density polyethylene. Copolymers of ethylene with vinyl acetate, ethyl acrylate, and acrylic acid are commercially important.

### Polyimides

Thermoset polyimides were introduced in the 1960s, followed in the early 1970s by thermoplastic polyimides. They are used in wire enamels, laminates, adhesives, gears, covers, bushings, piston rings, valve seats, and in solution form as a laminating varnish. Polyimides are characterized by repeating imide linkages: There are four types of aromatic polyimides: (1) condensation products made by the reaction pyromellitic dianhydride (PMDA)  $[C_6H_2(C_2O_3)_2]$  and aromatic diamines such as 4,4'-diaminodiphenyl ether  $[(C_6H_4NH_2)_2O]$ ; (2) condensation products of 3,4,3',4'-benzophenone tetracarboxylic dianhydride (BTDA)  $[(C_6H_2)_2CO(C_2O_3)_2]$  and aromatic amines; (3) the reaction of BTDA and a diisocyanate such as 4,4'-methylene-bis(phenylisocyanate)  $[OCNC_6H_4CH_2C_6H_4NCO]$ ; and (4) a polyimide based on diaminophenylindane and a dicarboxylic anhydride such as carbonyldiphthalic anhydride  $[OC_6H_4(CO)_2COC_6H_4(CO)_2]$ . Thermoset polyimides are produced in condensation polymers that possess reactive terminal groups capable of subsequent cross-linking through an addition reaction.

### Polyketones

The family of aromatic polyether ketones: polyetherketone (PEK), chemical structure; polyetheretherketone (PEEK), chemical structure ... and polyetherketoneketone (PEEKK).

### Polyphenylene Oxide, Modified

Engineering thermoplastic resins produced by the oxidative coupling of 2, 6-dimethylphenol  $[(CH_3)_2C_6H_3OH]$  (xlenol), then blended with impact polystyrene. Typical applications are electrical/electronic uses, business machine parts, appliances, and automotive parts.

### Polyphenylene Sulfide

Engineering thermoplastic resins produced by the reaction of p-dichlorobenzene  $[C_6H_4Cl_2]$  with sodium sulfide  $[Na_2S]$ . A thermoplastic, PPS exhibits excellent heat resistance, as well as outstanding chemical resistance, high stiffness and good retention of mechanical properties at elevated temperatures. The major use for polyphenylene sulfide is in electrical/ electronic parts and automotive parts.

### Polypropylene

Another "workhorse" of the plastics industry, polypropylene is one of the high-volume "commodity" thermoplastics. Polypropylene was developed out of the Nobel award-winning work of Karl Ziegler and Professor Natta in Europe, and came to the United States in 1957. It belongs to the "olefins" family, which also includes the polyethylenes, but it is quite

different in its properties. It has a low density, is fairly rigid, has a heat distortion temperature of 150 to 200 degrees F (making it suitable for "hot-fill" packaging applications), and excellent chemical resistance and electrical properties. Polypropylenes are also very easy to process in all conventional systems. (For information on processing methods, see: [processing methods](#).) Major applications of commercial PP are packaging, automotive, appliances and carpeting. Polypropylene is made by polymerizing propylene  $[\text{CH}_3\text{CHCH}_2]$  and in the case of copolymers with monomers, with suitable catalysts, generally aluminum alkyl and titanium tetrachloride mixed with solvents. The monomer unit in polypropylene is asymmetric and can assume two regular geometric arrangements: isotactic, with all methyl groups aligned on the same side of the chain, or syndiotactic, with the methyl groups alternating. All other forms, where this positioning is random, are called atactic. Commercial polypropylene contains 90-97% crystalline or isotactic PP with the remainder being atactic. Most processes remove excess atactic PP. This by-product is used in adhesives, caulks, and cablefilling compounds.

### Polystyrene

Styrene monomer and the polystyrene resin made from the monomer remained as chemical curiosities for 80 years following their discovery in 1845. It wasn't until 1925 when commercial production of styrene monomer began in Germany and the U.S. that polystyrene attracted interest, and it wasn't until after World War II when monomer capacity could be diverted from its essential wartime use for styrene-butadiene synthetic rubber that polystyrene became an important plastic. Today, polystyrene is among the most heavily used commodity thermoplastics. Foamed polystyrene is familiar to consumers as foam cups and containers, protective packaging and building insulation. Polystyrene is also widely used in other packaging and foodservice products, such as trays, disposable plates, cutlery and tumblers. Other applications include: automotive parts, toys, housewares, appliance parts, wall tiles, radio and TV housings, furniture, floats, luggage and many more. High molecular weight thermoplastic resins produced generally by the free-radical polymerization of styrene monomer  $[\text{C}_6\text{H}_5\text{CHCH}_2]$  which can be initiated by heating alone but more effectively by heating in the presence of free-radical initiator (such as benzoyl peroxide  $[(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2]$ ). Typical processing techniques are modified mass polymerization or solution polymerization, suspension polymerization, and expandable beads for foam.

### Polyurethanes

Introduced commercially in 1954, the urethanes have made an impact on a broad spectrum of U.S. industry. They are extremely versatile plastics in terms of the forms in which they are available: flexible or rigid foams,

solid elastomers (or rubbers), coatings, adhesives and sealants. Their versatility also extends to chemical structure in that, although the urethanes are generally considered to be thermosets, there are grades of urethane elastomers that are thermoplastic in nature and are supplied in pellet form for molding, calendaring and extrusion. Polyurethane's major and best known form, however, is a foamed or "cellular" material. Like all urethanes, the foams are prepared by first reacting two liquid components--polyols and isocyanates--together. In the presence of a blowing agent, this reaction will produce a foamed material having excellent thermal insulating properties, and, in fact, polyurethane foam is widely used in building insulation. The foams can either be soft and flexible or tough, and rigid, with all the possible variations in-between. Flexible foams have outstanding cushioning characteristics, excellent energy-absorbing properties and long life. They are used in furniture, cushioning, carpet underlay, bedding, packaging, textiles and automotive seating and safety padding. Rigid foams offer outstanding insulating values, excellent compressive strength, good dimensional stability and buoyancy. Besides building insulation, they are also found in refrigerators, trucks, boats (for flotation), and in the construction of furniture components. As coatings, polyurethanes impart excellent protective and decorative effects to wood, metals, rubber, textiles, concrete, paper, leather, other plastics and many other materials. In the form of elastomers, polyurethanes offer superior abrasion resistance and toughness, and are used in applications in which good performance and long service life are important: printing rolls, gaskets and seals, cable insulation, drive and conveyor belts, solid tires and automotive applications. Elastomers can also be processed by reaction injection molding, an important technique for producing automotive panels, front ends and bumpers. The commonly used isocyanates for manufacturing polyurethanes are toluene diisocyanate (TDI)  $[\text{CH}_3\text{C}_6\text{H}_3(\text{NCO})_2]$ , methylene diphenyl isocyanate (MDI)  $[\text{OCNC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{NCO}]$ , and polymeric isocyanates (PMDI), obtained by the phosgenation of polyamines derived from the condensation of aniline  $[\text{C}_6\text{H}_5\text{NH}_2]$  with formaldehyde (HCHO). Polyols (with hydroxyl groups) are macroglycols which are either polyester or polyether based. Polyurethane elastomers and resins take the form of liquid castings systems thermoplastic elastomers and resins, microcellular products, and millible gums.

### **Polyvinyl Acetate (PVAc) & Other Vinyls**

Polyvinyl acetate is a thermoplastic resin produced by the polymerization of vinyl acetate monomer  $[\text{CH}_3\text{COOCHCH}_2]$  in water producing an emulsion with a solids content of 50-55%. Most polyvinyl acetate emulsions contain co-monomers such as n-butyl acrylate, 2-ethyl hexyl acrylate, ethylene, dibutyl maleate and dibutyl fumarate. Polymerization of vinyl acetate with ethylene also can be used to produce solid vinyl

acetate/ethylene copolymers with more than 50% vinyl acetate content. Polyvinyl alcohol (PVOH) is produced by methanolysis or hydrolysis of polyvinyl acetates. The reaction can be controlled to produce any degree of replacement of acetate groups. Co-polymers of replaced acetate groupings and other monomers such as ethylene and acrylate esters are commercially important. Polyvinyl butyral (PVB) is made by reacting PVOH with butyraldehyde [ $\text{CH}_3(\text{CH}_2)_2\text{CHO}$ ]. Polyvinyl formal is made by condensing formaldehyde [ $\text{HCHO}$ ] in presence of PVOH or by the simultaneous hydrolysis and acetylation of PVAc. Polyvinylidene chloride is made by the polymerization of 1,1-dichloroethylene [ $\text{CH}_2\text{CCL}_2$ ]. Typical applications for the above resins are adhesives, paints, coatings and finishes, and packaging.

### Polyvinyl Chloride

The birth of polyvinyl chloride, or PVC or vinyl as it is better known to the public, dates back to a German patent in the 1910s, but it was not until the late 1920s that a technically useful product was introduced in the U.S. By the start of World War II, the significance of plasticizing PVC (that is, adding a chemical known as a plasticizer to make PVC flexible and processible) was fully realized. It was during the war that the real importance of this polymer became apparent when, due to the acute shortage of rubber, many companies turned to PVC and began to realize its advantages. Because of its wide use in applications that are close to consumers, such as upholstery, flooring, wall coverings, pipe, siding, apparel and accessories, vinyl is one of the better-known plastics. Vinyls are used mainly for their chemical and weathering resistance, high dielectric properties, or abrasion resistance. Vinyl is also dip molded into gloves, slush molded into boots and foamed to make calendered flooring, leather-like upholstery, shoe fabrics and carpet backing. Vinyls are thermoplastic resins produced by the polymerization of the gas vinyl chloride [ $\text{CH}_2\text{CHCl}$ ]. Under pressure, vinyl chloride becomes liquefied and is polymerized by one of four basic processes: suspension, emulsion, bulk, or solution polymerization. The pure polymer is hard, brittle and difficult to process, but it becomes flexible when plasticizers are added. A special class of PVC resin of fine particle size, often called dispersion grade resin, can be dispersed in liquid plasticizers to form plastisols. The addition of a volatile diluent or a solvent to the plastisol produces an organosol. Copolymers with vinyl acetate, vinylidene chloride, and maleate and fumarate esters find commercial application.

### Styrene Acrylonitrile

Thermoplastic copolymers of styrene [ $\text{C}_6\text{H}_5\text{CHCH}_2$ ] and acrylonitrile [ $\text{CH}_2\text{CHCN}$ ]. SAN resins are random, amorphous copolymers produced by emulsion, suspension, or continuous mass polymerization. Typical uses include automobile instrument panels and interior trim and

housewares.

### Styrene Butadiene Latexes & Other Styrene Copolymers

Styrene butadiene latexes usually have a resin content of about 50%. The styrene/butadiene ratio varies from 54:46 to 80:20. Most are carboxylated by the use of such acids as maleic [HOOCCHCHCOO], fumaric [HOOCCHCHCOOH], acrylic [CH<sub>2</sub>CHCOOH], or methacrylic [CH<sub>2</sub>C(CH<sub>3</sub>)COOH]. Two types of styrene-maleic anhydride (SMA) [(COCH)<sub>2</sub>O] are available: SMA copolymers, with and without rubber impact modifier (e.g., DYLARK<sup>®</sup>) and SMA terpolymer alloys (e.g., CADON<sup>®</sup>). K-Resin<sup>®</sup> is a solid styrenebutadiene copolymer resin. Acrylic monomers are also used in conjunction with styrene (or styrene plus other monomers) to produce specialty resins. For example, there are transparent terpolymers of methyl methacrylate, butadiene, and styrene (MBS), and others of acrylonitrile, an acrylic monomer, and styrene (AAS). Ion-exchange resins or divinylbenzene-modified polystyrene are another variation. SB latexes are used in carpet backing and paper coatings. The other styrenics are used in paints, coatings, and floor polishes, plus many other uses.

### Sulfone Polymers

A family of engineering thermoplastic resins characterized by the sulfone [SO<sub>2</sub>] group. Polysulfone is made by the reaction of the disodium salt of bisphenol A[(CH<sub>3</sub>)<sub>2</sub>C(C<sub>6</sub>H<sub>4</sub>OH)<sub>2</sub>] with 4,4'-dichlorodiphenyl sulfone 4,4'-DCDPS [(C<sub>6</sub>H<sub>4</sub>Cl)<sub>2</sub>SO<sub>2</sub>]. Polyethersulfone is made by the reaction of 4,4'-DCDPS with potassium hydroxide [KOH]. Polyphenylsulfone is similar to the other sulfone polymers. Typical applications for sulfone polymers are electrical/electronic uses and automotive parts.

### Thermoplastic Polyester (Saturated)

As molding and extrusion thermoplastic polyester compounds were introduced in the early 1970s, they quickly became important new members of the family of engineering thermoplastics. These linear polyesters are highly crystalline, hard, strong and extremely tough. The most familiar uses are soda bottles and textiles, but they are also used in X-ray film, magnetic tape (audio, video and computer); packaging; metallized film, strapping and labels. They form a family of polyesters in which the polyester backbones are saturated and hence unreactive. The most common commercial types are: PET (polyethylene terephthalate) produced by polycondensation of ethylene glycol [CH<sub>2</sub>OHCH<sub>2</sub>OH] with either dimethyl terephthalate (DMT) [C<sub>6</sub>H<sub>4</sub>(COOCH<sub>3</sub>)<sub>2</sub>] or terephthalic acid (TPA) [C<sub>6</sub>H<sub>4</sub>(COOH)<sub>2</sub>]; and PBT (polybutylene terephthalate) produced by the reaction of DMT with 1,4 butanediol [HO(CH<sub>2</sub>)<sub>4</sub>OH].

### Unsaturated Polyester

While this family of plastics goes under the name of “polyesters,” they are quite distinct from the polyesters described above. In fact, they are thermosets, and are probably most familiar to the public for their role in fiberglass reinforced plastics. These materials were introduced to military use (i.e., naval craft) in 1942. After World War II, their characteristics proved extremely appealing to such non-military markets as automotive, marine, corrosion-resistant structures, building, electrical applications, and consumer goods such as luggage, fishing poles and cases and housings of every type and description. These thermosetting resins are made by the condensation reaction between difunctional acids and glycols. The resulting polymer is then dissolved in styrene  $[C_6H_5CHCH_2]$  or other vinyl unsaturated monomer. The structures of the acids and glycols used and their proportions, especially the ratio of the unsaturated versus the saturated acid, and the type and amount of monomer used, are all tailored for each resin to balance economy, processing characteristics, and performance properties. One common formulation is the reaction of maleic anhydride  $[(COCH)_2O]$ , phthalic anhydride  $[C_6H_4(CO_2O)]$ , and propylene glycol  $[CH_3CHOHCH_2OH]$ . Both dicyclopentadiene  $[C_{10}H_{12}]$  and isophthalic acid  $[C_6H_4(COOH)_2]$  can be substituted for phthalic anhydride. Vinyl ester resins are linear reaction products of bisphenol A  $[(CH_3)_2C(C_6H_4OH)_2]$  and epichlorohydrin  $[CH_2OCHCH_2Cl]$  that are terminated with an unsaturated acid such as methacrylic acid  $[CH_2C(CH_3)COOH]$ .

### Urea-Formaldehyde

This plastic is another member of the amino family (as is melamine) and was developed in 1929. Like melamine, it is a very hard, scratch-resistant material with good chemical resistance, good electrical qualities and heat resistance up to 170 degrees F. Urea-Formaldehyde resins are formed by the condensation reaction of formaldehyde  $[HCHO]$  and urea  $[CO(NH_2)_2]$ . These thermoset resins are clear water-white syrups or white powdered materials which can be dispersed in water to form colorless syrups. They cure at elevated temperatures with appropriate catalysts. Molding powders are made by adding fillers to the uncured syrups, forming a consistency suitable for compression and transfer molding. The liquid and dried resins find extensive uses in laminates and chemically resistant coatings. The molding compounds are formed into rigid electrical and decorative products.

Sources: Chemical Economics Handbook, SRI International, Modern Plastics Encyclopedia, Whittington's Dictionary of Plastics, The Condensed Chemical Dictionary, [The SPI Plastics Engineering Handbook](#), The Story of the Plastics Industry (SPI).